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The short intermolecular contact (C—)H(3)···O(24), 2·47 (5) Å [$\frac{1}{2}+x, \frac{1}{2}-y, z$], with $d = 0{\cdot}23$ Å (Taylor & Kennard, 1982) probably forms a weak hydrogen bond; otherwise intermolecular distances correspond to or are greater than the relevant van der Waals radii.

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Structures of Two Isomeric Phenylethanolamine Analogs Containing the Benzobicyclo-[3.2.1]octane Skeleton

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Abstract. *endo*-8-Amino-6,7,8,9-tetrahydro-5,8-methano-5*H*-benzocyclohepten-9-ol hydrochloride, $C_{12}H_{16}NO^+.Cl^-$, $M_r = 225{\cdot}72$, tetragonal, $I4_1/a$, $a = b = 24{\cdot}641$ (3), $c = 7{\cdot}709$ (1) Å, $V = 4681$ (1) Å^3, $Z = 16$, $D_x = 1{\cdot}281$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}3032$ mm^{-1}, $F(000) = 1920$, $T = 297$ K. $R = 0{\cdot}0324$ for 1543 independent reflections collected. *exo*-8-Amino-6,7,8,9-tetrahydro-5,8-methano-5*H*-benzocyclohepten-9-ol, $C_{12}H_{15}NO$, $M_r = 189{\cdot}26$, monoclinic, $P2_1/c$, $a = 13{\cdot}863$ (3), $b = 6{\cdot}910$ (2), $c = 13{\cdot}437$ (3) Å, $V = 1018{\cdot}2$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}235$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}08456$ mm^{-1}, $F(000) = 408$, $T = 297$ K. $R = 0{\cdot}0378$ for 1340 independent reflections collected. The torsion angles N—C(8)—C(9)—C(9a) of the two isomers are 174·0 (2) and 173·4 (1)°, respectively, which are very close to those observed for epinephrine (172°) and norepinephrine (179°) with the side chain in a fully extended conformation. The cyclohexene moiety has a half-chair conformation as found in tetralols.

Introduction. In the continuation of our effort in studying the relationship between conformation and biological activities in phenylethanolamine analogs (Grunewald, Reitz, Hallett, Rutledge, Vollmer, Archuleta & Ruth, 1980; Rafferty & Grunewald, 1982; Grunewald, Pleiss & Rafferty, 1982), we obtained *endo*- and *exo*-8-amino-6,7,8,9-tetrahydro-5,8-methano-5*H*-benzocyclohepten-9-ols (1) and (2). They are both conformationally defined analogs of phenyl-

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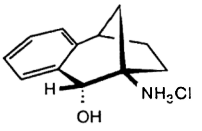
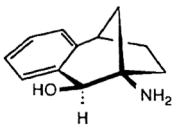
ethanolamine. In order to assign the stereochemistry of the hydroxyl group in the two isomers unambiguously, we carried out X-ray crystallographic studies on each isomer.



(1)



(2)

Experimental. *endo*-8-Amino-6,7,8,9-tetrahydro-5,8-methano-5*H*-benzocycloheptен-9-ol hydrochloride [compound (1)] was obtained by recrystallization from ethanol and ether as colorless tetragonal prisms and *exo*-8-amino-6,7,8,9-tetrahydro-5,8-methano-5*H*-benzocycloheptен-9-ol [compound (2)] was recrystallized from methylene chloride as colorless plates. Each crystal was mounted on a glass fiber oriented approximately along [001] for (1) or [100] for (2). Cell constants were determined using 15 centered reflections widely scattered throughout reciprocal space. Full spheres of data out to $2\theta = 45°$ were collected using a Syntex $P2_1$ diffractometer (Mo $K\alpha$, graphite monochromator) with θ–2θ scan mode. Corrections were made in intensity of two [for (2)] or three [for (1)] standard reflections monitored every 100 measurements. Independent F_o^2 data were obtained by merging equivalent reflections. The reflections with $F_o^2 < 0{\cdot}2\sigma(F_o^2)$ were reset to $F_o^2 = 0{\cdot}2\sigma(F_o^2)$. All reflections were used in subsequent calculations. The structures were solved by the direct method using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All H atoms were located from the difference Fourier maps. Full-matrix refinement, anisotropic for non-H and isotropic for H atoms. Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The final difference Fourier maps were featureless [$\pm 0{\cdot}17$ e Å^{-3} for (1) and $\pm 0{\cdot}26$ e Å^{-3} for (2)]. The Δ/σ of the last cycle of least squares was less than 0·13 for (1) and 0·76 for (2). Atomic scattering factors were taken from *International Tables for X-ray Crystallography*

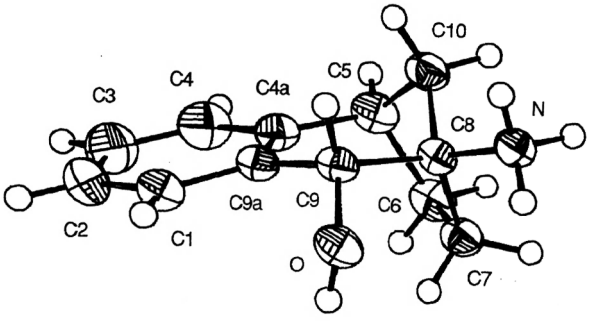
Table 1. *Summary of data-collection and processing parameters*

	Compound (1)	Compound (2)
Crystal size (mm)	0·3 × 0·3 × 0·5	0·3 × 0·3 × 0·1
Range of *hkl*	−26→26, 0→26, 0→8	0→14, 0→7, −14→10
R_{int}	0·018	0·029
Total reflections	3891	2857
Independent reflections	1543	1340
Total variables	201	188
R	0·0324	0·0378
wR	0·0314	0·0493
S	1·182	0·9770

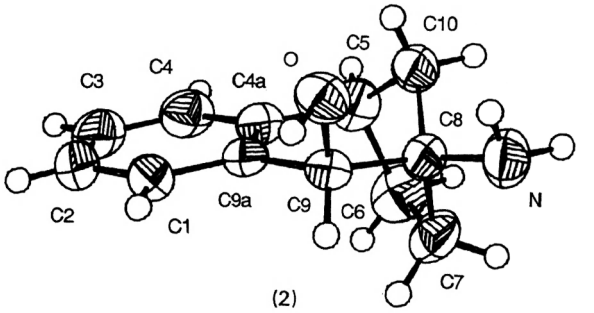
Table 2. *Fractional coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms*

$$B_{eq} = \tfrac{8}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Compound (1)				
Cl	0·03911 (2)	0·37277 (2)	0·22687 (6)	3·09
N	0·58881 (7)	0·26438 (8)	0·1239 (2)	2·59
O	0·58277 (5)	0·28830 (6)	−0·2364 (2)	2·89
C(1)	0·65966 (9)	0·36680 (8)	−0·3821 (3)	3·13
C(2)	0·7024 (1)	0·39358 (9)	−0·4612 (3)	4·07
C(3)	0·7518 (1)	0·3972 (1)	−0·3795 (3)	4·46
C(4)	0·75927 (9)	0·37317 (9)	−0·2205 (3)	3·97
C(4a)	0·71724 (8)	0·34589 (7)	−0·1377 (3)	2·87
C(5)	0·72594 (8)	0·31688 (8)	0·0328 (3)	3·09
C(6)	0·73240 (8)	0·25579 (9)	0·0011 (3)	3·27
C(7)	0·67419 (8)	0·23580 (8)	−0·0284 (3)	2·81
C(8)	0·63778 (7)	0·28356 (7)	0·0271 (2)	2·29
C(9)	0·61861 (7)	0·31774 (8)	−0·1260 (2)	2·35
C(9a)	0·66647 (7)	0·34340 (7)	−0·2188 (2)	2·56
C(10)	0·67400 (8)	0·31889 (9)	0·1396 (3)	2·79
Compound (2)				
N	0·3775 (2)	−0·2720 (3)	0·1081 (2)	4·68
O	0·3933 (1)	0·0864 (2)	0·1971 (1)	4·01
C(1)	0·3467 (2)	0·1312 (3)	0·3879 (2)	3·90
C(2)	0·2808 (2)	0·2011 (3)	0·4261 (2)	4·83
C(3)	0·1622 (2)	0·1395 (3)	0·3656 (2)	5·09
C(4)	0·1100 (2)	0·0132 (3)	0·2667 (2)	4·69
C(4a)	0·1748 (2)	−0·0584 (3)	0·2271 (2)	3·65
C(5)	0·1202 (2)	−0·2027 (3)	0·1211 (2)	4·46
C(6)	0·1651 (2)	−0·4052 (3)	0·1748 (3)	5·56
C(7)	0·2939 (2)	−0·4119 (3)	0·2115 (2)	4·64
C(8)	0·3059 (2)	−0·2316 (3)	0·1519 (2)	3·55
C(9)	0·3697 (2)	−0·0696 (2)	0·2483 (2)	3·09
C(9a)	0·2955 (2)	0·0003 (2)	0·2893 (2)	3·15
C(10)	0·1737 (2)	−0·1715 (3)	0·0519 (2)	4·07



(1)



(2)

Fig. 1. *ORTEP*II (Johnson, 1976) drawings of (1) and (2). Non-H atoms are displayed as principal ellipses at the 50% probability level, H atoms as small spheres of arbitrary size.

Table 3. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *involving non-*H *atoms, with their e.s.d.'s in parentheses*

	Compound (1)	Compound (2)		Compound (1)	Compound (2)		Compound (1)	Compound (2)
N–C(8)	1·495 (2)	1·458 (4)	C(4)–C(4a)	1·390 (3)	1·386 (4)	C(6)–C(7)	1·534 (3)	1·535 (4)
O–C(9)	1·425 (2)	1·421 (3)	C(4a)–C(5)	1·512 (3)	1·509 (3)	C(7)–C(8)	1·540 (3)	1·545 (3)
C(1)–C(2)	1·384 (3)	1·382 (5)	C(4a)–C(9a)	1·400 (3)	1·397 (3)	C(8)–C(9)	1·525 (3)	1·521 (2)
C(1)–C(9a)	1·395 (3)	1·388 (3)	C(5)–C(6)	1·533 (3)	1·522 (3)	C(8)–C(10)	1·519 (3)	1·524 (2)
C(2)–C(3)	1·375 (4)	1·382 (4)	C(5)–C(10)	1·522 (3)	1·518 (4)	C(9)–C(9a)	1·517 (3)	1·512 (4)
C(3)–C(4)	1·373 (4)	1·369 (3)						
C(2)–C(1)–C(9a)	120·2 (2)	120·9 (2)	C(6)–C(5)–C(10)	101·9 (2)	102·1 (2)	C(9)–C(8)–C(10)	107·9 (2)	108·0 (2)
C(1)–C(2)–C(3)	120·2 (2)	119·6 (2)	C(5)–C(6)–C(7)	104·0 (2)	103·8 (2)	O–C(9)–C(8)	111·9 (2)	109·3 (2)
C(2)–C(3)–C(4)	120·0 (2)	120·0 (3)	C(6)–C(7)–C(8)	105·0 (2)	106·4 (2)	O–C(9)–C(9a)	114·4 (2)	110·1 (2)
C(3)–C(4)–C(4a)	121·2 (2)	121·2 (2)	N–C(8)–C(7)	111·5 (2)	111·7 (2)	C(8)–C(9)–C(9a)	110·7 (1)	112·0 (2)
C(4)–C(4a)–C(5)	121·5 (2)	122·0 (2)	N–C(8)–C(9)	108·1 (1)	107·5 (2)	C(1)–C(9a)–C(4a)	119·5 (2)	119·1 (2)
C(4)–C(4a)–C(9a)	118·9 (2)	119·2 (2)	N–C(8)–C(10)	111·8 (2)	116·4 (2)	C(1)–C(9a)–C(9)	120·3 (2)	119·3 (2)
C(5)–C(4a)–C(9a)	119·6 (2)	118·8 (2)	C(7)–C(8)–C(9)	112·8 (2)	110·1 (2)	C(4a)–C(9a)–C(9)	120·2 (2)	121·5 (2)
C(4a)–C(5)–C(6)	109·9 (2)	109·7 (2)	C(7)–C(8)–C(10)	104·7 (2)	103·0 (2)	C(5)–C(10)–C(8)	99·6 (2)	101·3 (2)
C(4a)–C(5)–C(10)	109·6 (2)	109·5 (2)						
C(9a)–C(1)–C(2)–C(3)	0·2 (3)	0·2 (3)	C(4)–C(4a)–C(9a)–C(9)	−175·3 (2)	−178·6 (2)	N–C(8)–C(9)–C(9a)	174·0 (2)	173·4 (1)
C(2)–C(1)–C(9a)–C(4a)	−1·8 (3)	1·0 (3)	C(5)–C(4a)–C(9a)–C(1)	−175·3 (2)	−179·2 (2)	C(7)–C(8)–C(9)–O	66·7 (2)	173·0 (1)
C(2)–C(1)–C(9a)–C(9)	175·4 (2)	178·7 (2)	C(5)–C(4a)–C(9a)–C(9)	7·5 (3)	3·2 (3)	C(7)–C(8)–C(9)–C(9a)	−62·2 (2)	−64·7 (2)
C(1)–C(2)–C(3)–C(4)	1·4 (4)	−1·4 (3)	C(4a)–C(5)–C(6)–C(7)	−77·9 (2)	−78·9 (2)	C(10)–C(8)–C(9)–O	−178·1 (1)	−75·3 (1)
C(2)–C(3)–C(4)–C(4a)	−1·2 (4)	1·4 (3)	C(10)–C(5)–C(6)–C(7)	38·3 (2)	37·1 (2)	C(10)–C(8)–C(9)–C(9a)	53·0 (2)	47·0 (2)
C(3)–C(4)–C(4a)–C(5)	176·7 (2)	178·0 (2)	C(4a)–C(5)–C(10)–C(8)	66·9 (2)	67·4 (2)	N–C(8)–C(10)–C(5)	163·1 (2)	163·3 (2)
C(3)–C(4)–C(4a)–C(9a)	−0·4 (3)	−0·2 (3)	C(6)–C(5)–C(10)–C(8)	−49·5 (2)	−48·8 (2)	C(7)–C(8)–C(10)–C(5)	42·2 (2)	40·8 (2)
C(4)–C(4a)–C(5)–C(6)	−100·5 (2)	−100·2 (2)	C(5)–C(6)–C(7)–C(8)	−11·9 (2)	−11·7 (2)	C(9)–C(8)–C(10)–C(5)	−78·3 (2)	−75·7 (2)
C(4)–C(4a)–C(5)–C(10)	148·3 (2)	148·6 (2)	C(6)–C(7)–C(8)–N	−139·9 (2)	−143·6 (2)	O–C(9)–C(9a)–C(1)	39·0 (2)	−65·8 (2)
C(9a)–C(4a)–C(5)–C(6)	76·6 (2)	78·0 (2)	C(6)–C(7)–C(8)–C(9)	98·2 (2)	97·0 (2)	O–C(9)–C(9a)–C(4a)	−143·8 (2)	111·8 (2)
C(9a)–C(4a)–C(5)–C(10)	−34·6 (2)	−33·3 (2)	C(6)–C(7)–C(8)–C(10)	−18·9 (2)	−17·9 (2)	C(8)–C(9)–C(9a)–C(1)	166·6 (2)	172·3 (2)
C(4)–C(4a)–C(9a)–C(1)	1·9 (3)	−1·0 (3)	N–C(8)–C(9)–O	−57·1 (2)	51·1 (2)	C(8)–C(9)–C(9a)–C(4a)	−16·3 (2)	−10·1 (2)

(1974). All calculations were performed on a Honeywell 66/6000 computer or a VAX 8600 computer at the University of Kansas using programs in the *KUDNA* system (Takusagawa, 1984). Other experimental details are summarized in Table 1.

Discussion. Final atomic parameters are given in Table 2. Bond lengths, bond angles and torsion angles are listed in Table 3.* Views of (1) and (2) with the atomic numbering are presented in Fig. 1.

The crystal structures of biologically active norepinephrine (Andersen, 1975) and epinephrine (Carlstrom & Bergin, 1967) have been reported with the catechol and amino group of the ethanolamine side chain in a fully extended conformation. The phenylethanolamine moiety embedded in our conformationally defined analogs (1) and (2) assumes this conformation as indicated by the torsion angles N–C(8)–C(9)–C(9a).

2-Amino-1-tetralols may be considered as conformationally restricted analogs of phenylethanolamine. The cyclohexene moiety in 2-amino-1-tetralol derivatives adopts a half-chair conformation with the amino group in an equatorial orientation in crystals (Motohashi, Wada, Kamiya & Nishikawa, 1980; Hambley & Rodgers, 1986). The 2-amino-1-tetralol moiety in (1) and (2) has a similar half-chair conformation for the cyclohexene ring with the primary amine occupying an equatorial position and the hydroxyl group occupying a pseudo-equatorial one in the *endo* isomer (1) or a pseudo-axial one in the *exo* isomer (2).

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44339 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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